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Study of the adsorption of oxalic acid on rice bran in aqueous solution

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ABSTRACT

The adsorption of oxalic acid on the rice bran was studied under various conditions such as temperature, contact time, adsorbant dose and concentration of adsorbate. Batch adsorption experiments were conducted and the result showed that the adsorption was dependent on all these parameters. The adsorption process obeys the Langmuir and Freundlich adsorption isotherms. By these adsorption isotherms, thermodynamics adsorption parameters and kinetics adsorption parameters were calculated.

KEYWORDS

Adsorption;
Isotherm;
Rice bran;
Thermodynamics;
Kinetics

INTRODUCTION

Sorption (adsorption, ion-exchange, complexation, etc.) utilizing low-cost filter media could be an attractive option for small businesses, industry, or municipalities to treat wastewater or runoff. Several workers have reported on the potential use of agricultural by–products as good substrates for the removal of metal ions from aqueous solutions and wastewaters. This process attempts to put into use the principle of using waste to treat waste and become even more efficient because these agricultural by–products are readily available and often pose waste disposal problems. Hence, they are available at little or no cost, since they are waste products. This makes the process of treating wastewaters with agricultural by–product adsorbents more cost effective than the use of conventional adsorbents like activated carbon. In addition, there is no need for complicated regeneration process when using agricultural by–products for wastewater treatment[1-10].

Rice bran is one of the important agricultural wastes. In this study is used from it as adsorbent. The outer coating of a rice grain is the rice bran. It is the brown layer between the hull and the white rice. The hull and bran layer is the discarded byproduct during the milling process to make white rice. The rice bran is a beneficial source of lots of lignin, cellulose and silica with adequate adsorptive capacity that can be use as a sorbent[11]. Dicarboxylic acids are important compounds in biochemistry, nature and industry. Oxalic acid is one of the derivatives of dicarboxylic acids by m.p of 189-191 °C and density of 1.90 g.cm^{-3}. Ion- exclusion chromatography (IEC) coupled with electrospray ionization quadropole mass spectroscopy (ESI-MS) has been used for the analysis of oxalic acid[12]. Removal methods of organic componds in industrial discharges may be traditionally divided into three main categories: physical, chemical, and biological processes. Among them, physical adsorption is generally considered to be the most efficient method for quickly lowering the concentration of dissolved organic componds in the solution[13-16]. Thus, the main objectives of this work were to characterize the physical properties of rice bran to examine its adsorption behaviors of removing oxalic acid from aqueous solution. Batch experiments were conducted to investigate the effects of adsorbent dosage, absorbate concentration, contact time and temperature on the adsorption of oxalic acid on the rice bran. Lngmuir and Freundlich isotherm models were used to illustrate the experimental isotherms models and isotherms constants. The rate of adsorption was found to obey the rule of second order model with good correlations.

EXPERIMENTAL

All the chemicals were purchased from Merck. Before the process of adsorption characterization the rice bran must be prepared. Thus, the amounts which are needed was mixed with distilled water by stirrer-magnet for 1 hr. Then it was washed with distilled water until a pH of 7.0 was attained, dried in an oven at 50°C for 24 hr and stored in the desiccators. It was further crushed, grined and sieved to two different size (average size <0.5 mm and average size between 0.5 and 1mm) in accordance with the American Society for Testing and Materials (ASTM). All experiments were carried out by the samples containing 50 cc of different initial concentration (0.01- 0.04 M) of oxalic acid in the range of 28-60°C temperature. 4 g of the adsorbent was transferred into various 250 ml Erlenmeyer flask and oxalic acid solution by fixed concentration was added and mixed using a stirrer- magnet for 1 hr. Then the solution was filtered its concentration was determined by titration with 0.04 M solution of NaOH. The amount of equilibrium adsorption, *q*e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W}$$

where *C*0 and *C*e (mg/l) are the liquid-phase concentrations of oxalic acid at initial and equilibrium, respectively. *V*(l) is the volume of the solution and *W*(g) is the the mass of dry adsorbent used[17].

Effect of adsorbate concentration

Several stock solutions with concentration (0.01-0.04 M) were prepared. Each solution was added to 4.0 g of the adsorbent in different 250 ml flasks and agitated using a mechanical agitator for 1 hr each. At the end of the time, the contents of the flasks were filtered and analyzed. The results are shown in figure 1.

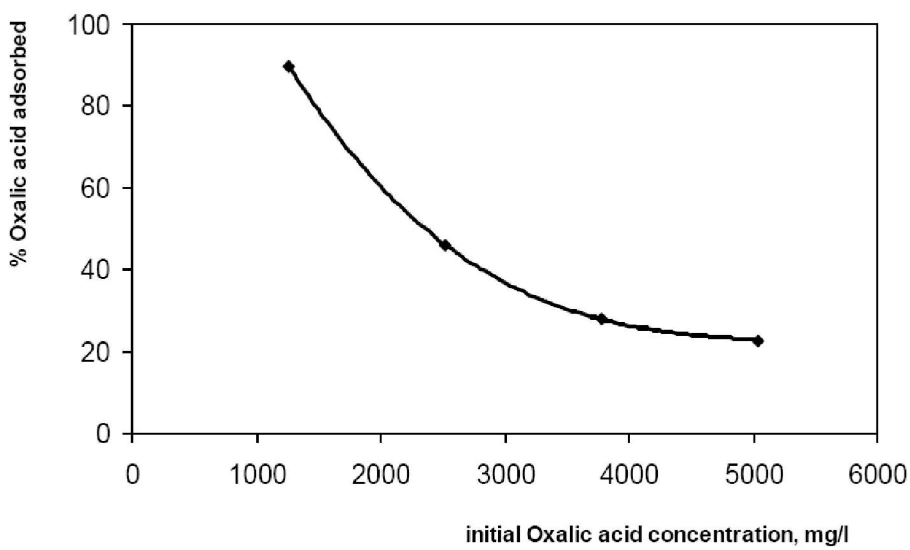

Figure 1 : Influence of initial oxalic acid concentration on adsorption of oxalic acid on rice bran

Effect of adsorbent dose

50 ml each of the oxalic acid solutions were added to various amount of the adsorbent (1-7.0 g) in different 250 ml flasks, flasks were agitated for 1hr on a mechanical stirrer. The content of the flask was filtered and analyzed. The results are presented in figure 2.

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Effect of contact time

50 ml each of stock solution of oxalic acid was transferred into different 250 cm^3 Erlenmeyer flask, corked and labeled. 4.0 g each of the adsorbent was weighed into the different labeled flasks and agitated in a shaker for different contact times (3, 5, 7, 10, 15, 20, 45 and 60 minutes). After each agitated time, the content of each flask was then filtered. The equilibrium concentration of the metal in each of the filtrate was determined. The results obtained are shown in figure 3.

Effect of temperature

50 ml each of stock solution was transferred into various 250 cm^3 flask containing 4.0 g each of the adsorbent, corked and labeled for different temperatures 28, 45, 50, 60°C respectively. The mixture was heated and shaken to the appropriate temperature in a water bath. At the right temperature, the content of the each of the flask was removed, filtered and analyzed. The results obtained are shown in figure 4.

RESULT AND DISCUSSION

The concentration-dependent data for the adsorption of oxalic acid is presented in figure 1. It was found that the percentage oxalic acid removal decreased with increase in initial oxalic acid concentration. This can be explained by the fact that more adsorption sites were

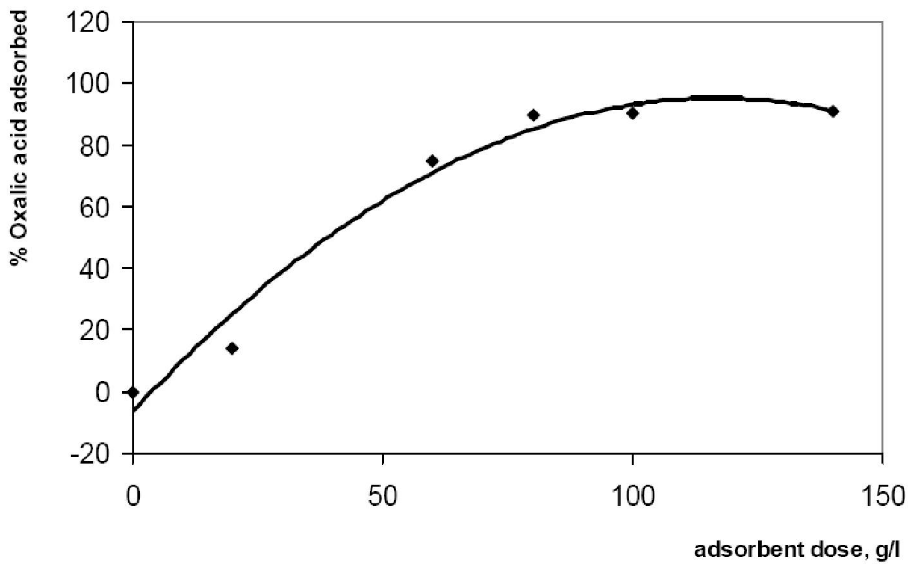

Figure 2 : Influence of adsorbent dose on adsorption of oxalic acid on rice bran with a particle size of d < 0.5 mm

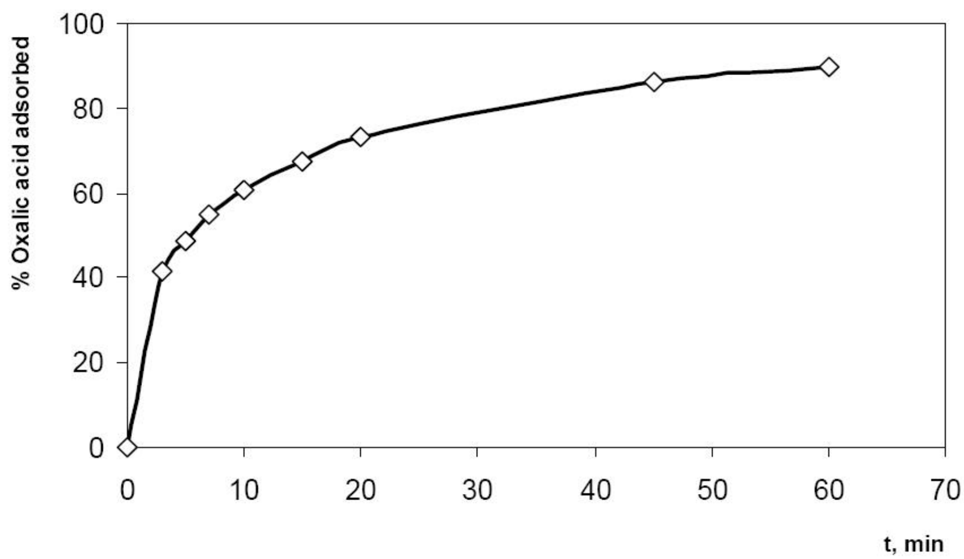

Figure 3 : Influence of contact time on adsorption of oxalic acid on rice bran

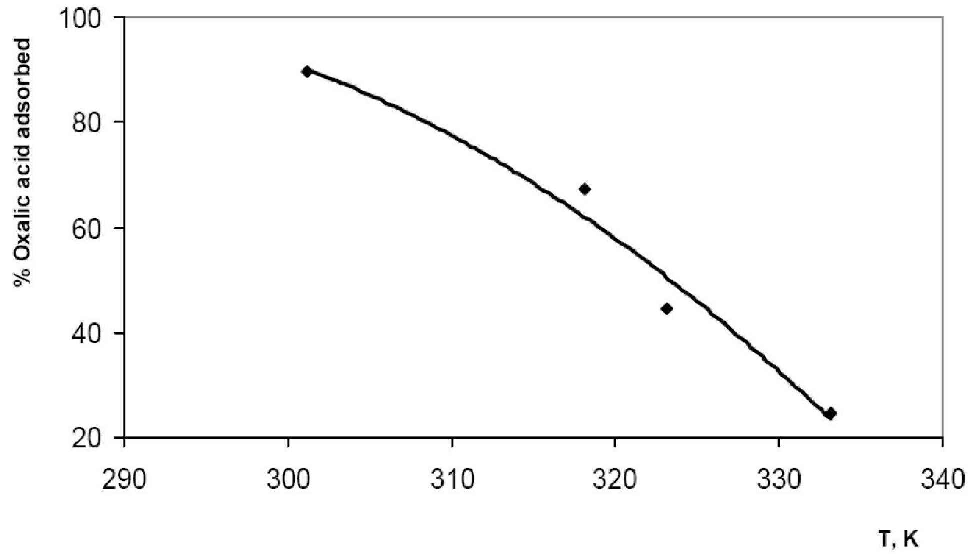

Figure 4 : Influence of temperature on adsorption of oxalic acid on rice bran

being covered as the oxalic acid concentration increases.

The effect of the adsorbent dose on the removal of oxalic acid from aqueous solution was investigated by varying the dose of the adsorbent from 1 – 7.0 g. It is expected that an increase in the dosage of adsorbent should yield a corresponding increase in the amount of oxalic acid adsorbed on the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore competition for bonding sites between molecules of the adsorbate should decrease with increase in dose of the adsorbent[18,19]. From figure 2 this trend was inconsistent and therefore suggests that the use of rice bran as adsorbent partly depend on its dose in aqueous solution. Further increase of adsorbent dose did not cause any significant change because equilibrium was achieved between solution and solid phase.

The result obtained from time-dependent experiments for the adsorption of oxalic acid on rice bran was presented in figure 3. As the contact time was increased, the amount of oxalic acid removed also increased. The data showed oxalic acid removal from aqueous solution increases initially until equilibrium was attained and then was constant. In according to figure 3, the observable time for maximum adsorption is between 50-60 minutes.

The effect of temperature on the removal of oxalic acid from aqueous solution was investigated by varying the temperature of adsorption between 28°C and 60°C (figure 4). The data showed that with increasing temperature the amount of oxalic acid adsorbed on the surface of the adsorbent decreases. The attractive forces between the adsorbent and the adsorbate ion may have been weakened making the adsorption to decrease. At high temperature, the thickness of the boundary layer is expected to decrease due to the increased tendency of the ions to escape from the surface of the adsorbent to the solution phase hence there is bound to be weak adsorption interactions between the adsorbent and the adsorbate.

Adsorption isotherms

Adsorption is usually described through isotherms, that is the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. In this manner, the Langmuir and the Freundlich isotherm equations were used to interpret the experimental data. The first mathematical fit to an isotherm was published by Freundlich and Küster (1894):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where Ce is the equilibrium concentration of the solute (mg/L) and qe is the equilibrium adsorption capacity (mg/g). The Freundlich isotherm constants KF and $1/n$ can be calculated from the plot of ln$q$e versus ln$C$e. The slope ($1/n$) measures the surface heterogeneity. Heterogeneity becomes more prevalent as $1/n$ gets closer to zero.

Lngmuir equation is a semi-empirical isotherm de-

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rived from a proposed kinetic mechanism. It is based on four assumptions[20]:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The linearized form of the Langmuir adsorption isotherm equation is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

The Langmuir constants, which are *q*m and *K*L values, can be calculated from the plot *C*e/*q*e versus *C*e. The maximum adsorption capacity was determined as 3.21 mg/g at 28°C. Isotherm models constants and correlation coefficients for oxalic acid adsorption on rice bran listed in TABLE 1. The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in TABLE 1. The correlation coefficient shows that the adsorption process could be described by the both Langmuir and Freundlich model equation. The Langmuir constants (q_m and K_L) values were fit the experimental data.

TABLE 1 : Isotherm Models Constants and Correlation Coefficients for oxalic acid adsorption on rice bran

	Freundlich			Langmuir		
T, K	K_f, mg/g	n, mg/l	R^2	K_L, l/mg	q_m, mg/g	R^2
301.15	0.177	13.33	0.994	0.013	3.21	0.999

Thermodynamic studies

Thermodynamic parameters such as change in Gibb's free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°) were determinated using the following equations:

$$\ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where m is the adsorbent dose (mg/l), C_e is the equilibrium concentration (mg/l) of the oxalic acid in solution, R is the gas constant (8.314 J/mol/K) and T is the temperature (K). ΔG°, ΔH° and ΔS° are changes in Gibb's free energy (J/mol), enthalpy (J/mol), entropy (J/mol/K), respectively. The values of ΔH° and ΔS° were determined from the slopes ($-\Delta H^\circ/R$) and the intercepts ($\Delta S^\circ/R$) of the plots of $\ln\left(\frac{q_e m}{C_e}\right)$ vs.1/T. The values of thermodynamic parameters are presented in TABLE 2. The negative values of ΔG° indicate that the adsorption process is feasible and spontaneous in nature. The negative value of ΔH° suggest the exothermic nature of adsorption and the negative value of ΔS° described the randomness at the adsorbent-solution interface decreased during the adsorption.

TABLE 2 : Thermodynamic parameters for oxalic acid adsorption on rice bran

ΔS°, kJ/mol.K^{-1}	ΔH°, kJ/mol	ΔG°, kJ/mol
-0.02673	-10.322	-2.67

Sorption kinetics

Sorption kinetics was studied for adsorption of oxalic acid on rice bran of initial concentration 0.01 mol/l. Figure 3 Shows that the rate of sorption decrease with increase of time and after 60 min, equilibrium was achieved. Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution on to an adsorbent. The rate constant of adsorption was determined from the pseudo-first order rate expression following equation given by Lagergren:

$$\ln(q_e - q_t)_t = \ln q_e - k_{ad} t$$

Where k_{ad} is the rate constant of adsorption (mim^{-1}), q_e and q_t are the amount of oxalic acid adsorbed at equilibrium and at time t (mg/g) respectively. The values of the k_{ad} and q_e^{cal} were calculated from the slopes ($-k_{ad}$) and the intercepts (ln q_e) of the plots of ln (q_e-q_t) vs. t reported in TABLE 3. TABLE 3 shows that there is a large difference in the values of q_e^{cal} and $q_e^{exp.}$ The rate constant of adsorption was also determined from the pseudo-second order rate expression[21]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

Where k_2 is the rate constant of adsorption (g/mg/min). The values of k_2 and q_e^{cal} were calculated from the intercepts ($1/k_2 qe^2$) and the slopes ($1/q_e$) of the plots of t/q_e vs. t. respectively, reported in TABLE 3. The results show that the values of q_e^{cal} and q_e^{exp} are almost equal and regression correlation coefficient (R^2) is close to unity which confirm that adsorption of oxalic acid on rice bran follows pseudo-second order kinetic model.

TABLE 3 : Kinetic parameters for oxalic acid adsorption on rice bran

Pseudo-first order				Pseudo-second order			
q_e^{exp}, mg/g	q_e^{cal}, mg/g	K_{ad}, min^{-1}	R^2	q_e^{exp}, mg/g	q_e^{cal}, mg/g	K_2, g/mg.min	R^2
2.44	1.5	0.06	0.99	2.44	2.63	0.07	0.99

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